

# Theory of NMR chemical shift in an electronic state with arbitrary degeneracy

Willem Van den Heuvel and Alessandro Soncini\*  
School of Chemistry, University of Melbourne, VIC 3010, Australia

We present a theory of nuclear magnetic resonance (NMR) shielding tensors for electronic states with arbitrary degeneracy. The shieldings are here expressed in terms of generalized Zeeman ( $g^{(k)}$ ) and hyperfine ( $A^{(k)}$ ) tensors, of all ranks  $k$  allowed by the size of degeneracy. Contrary to recent proposals [T. O. Pennanen and J. Vaara, Phys. Rev. Lett. **100**, 133002 (2008)], our theory is valid in the strong spin-orbit coupling limit. Ab initio calculations for the 4-fold degenerate  $\Gamma_8$  ground state of lanthanide-doped fluorite crystals  $\text{CaF}_2:\text{Ln}$  ( $\text{Ln} = \text{Pr}^{2+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ , and  $\text{Dy}^{3+}$ ) show that previously neglected contributions can account for more than 50% of the paramagnetic shift.

**Introduction.** Paramagnetic nuclear magnetic resonance (pNMR) spectroscopy is a fundamental tool for probing static *and* dynamic *local* magnetic properties of materials [1] and metallo-proteins [2]. pNMR plays a central role in the elucidation of the quantum dynamics of single-molecule magnets and antiferromagnetic spin rings [3]. Moreover, it is an increasingly central technique for probing *strong spin-orbit coupled* electronic states in a dissipative environment, as shown by a recent study of quantum tunneling processes [4], silent in ac-susceptibility experiments, in lanthanide-based ( $\text{Dy}^{3+}$  and  $\text{Tb}^{3+}$ ) molecular nanomagnets.

Despite the central role of pNMR in the development of new magnetic materials, only very recently ab initio approaches have been developed for the calculation of fundamental pNMR observables, such as nuclear shielding tensors [5]. In particular, by generalizing the work of Moon and Patchkovskii [6] on Kramers doublets, the paper by Pennanen and Vaara [7] stands out as the first comprehensive formulation of NMR shielding tensors in terms of molecular response properties, like the second-rank (first-rank in spin) EPR  $\mathbf{g}$  and hyperfine  $\mathbf{A}$  tensors, routinely computed via ab initio methods [5, 7–10]. The work by Pennanen and Vaara [7] aims at proposing an NMR-theory for arbitrary electronic ground state degeneracy. However, this task is only accomplished in [7] for the weak spin-orbit coupling limit, and to date *no theory fully accounts for truly general (spin and orbital) electronic degeneracy*, as that arising in strong spin-orbit coupled lanthanide nanomagnets.

In this Letter we propose a general theory for the ab initio calculation of pNMR chemical shifts as function of molecular tensors of all ranks consistent with the size of degeneracy, which applies to arbitrarily strong spin-orbit coupling (SOC) limit, and any degree of electronic degeneracy.

**Theory.** In the linear response regime, the electron-induced magnetic field  $\mathbf{B}_{\text{ind}}^I$  experienced by a nucleus  $I$  in a molecule immersed in a magnetic field  $\mathbf{B}$ , is proportional to the field itself, so that  $\mathbf{B}_{\text{ind}}^I = -\mathbf{B} \cdot \boldsymbol{\sigma}^I$ . This leads to an electron-mediated interaction energy between external field and the magnetic dipole moment  $\boldsymbol{\mu}^I$  of nucleus  $I$  which is bilinear in the field and the nuclear

dipole, given by  $W^{\mathbf{B}, \boldsymbol{\mu}^I} = -\mathbf{B}_{\text{ind}}^I \cdot \boldsymbol{\mu}^I$ . The proportionality tensor  $\boldsymbol{\sigma}^I$  is the NMR shielding tensor, its trace being related to the chemical shift of nucleus  $I$ .

In a system with a degenerate ground state, the energy  $W^{\mathbf{B}, \boldsymbol{\mu}^I}$  must be averaged among the thermally accessible states resulting from the splitting of the degeneracy under the experimental conditions, leading to  $\langle W^{\mathbf{B}, \boldsymbol{\mu}^I} \rangle = -\langle \mathbf{B}_{\text{ind}}^I \rangle \cdot \boldsymbol{\mu}^I = B_\alpha \langle \sigma_{\alpha\beta}^I \rangle \mu_\beta^I$ , where Greek indices correspond here to Cartesian tensor components, and a sum is implied over repeated indices. Then the field-independent shielding tensor is defined as

$$\langle \sigma_{\alpha\beta}^I \rangle = \left. \frac{\partial^2 \langle W^{\mathbf{B}, \boldsymbol{\mu}^I} \rangle}{\partial B_\alpha \partial \mu_\beta^I} \right|_{\mathbf{B} \rightarrow 0} = - \left. \frac{\partial \langle B_{\text{ind},\beta}^I \rangle}{\partial B_\alpha} \right|_{\mathbf{B} \rightarrow 0}. \quad (1)$$

A strategy to evaluate Eq. (1) in transition metal complexes has been first discussed in [11]. Here we reformulate this strategy in terms of projection operators.

We label  $H_0$  the unperturbed Hamiltonian in the absence of the time-odd fields  $\mathbf{B}$  and  $\boldsymbol{\mu}^I$ . The well-known microscopic operators [12], linear and bilinear in  $\mathbf{B}$  and  $\boldsymbol{\mu}^I$ , describing the interaction between electrons and fields are given by [13] (i) the Zeeman term  $\mathcal{H}_z = -\boldsymbol{\mu}_e \cdot \mathbf{B}$  where  $\boldsymbol{\mu}_e$  is the electronic magnetic moment and (ii) the four Ramsey terms, describing the interaction between the electrons and  $\boldsymbol{\mu}^I$ . The Ramsey terms can be further partitioned in a contribution linear in  $\boldsymbol{\mu}^I$ , and a contribution that is bilinear in  $\mathbf{B}$  and  $\boldsymbol{\mu}^I$ . We collect the terms linear in  $\boldsymbol{\mu}^I$  in  $\mathcal{F}_\beta^I \mu_\beta^I$ , where the time-odd operator  $\mathcal{F}_\beta^I = \mathcal{F}_{1,\beta}^I + \mathcal{F}_{2,\beta}^I + \mathcal{F}_{3,\beta}^I$  is the sum of the nuclear-orbit ( $\mathcal{F}_{1,\beta}^I$ ), Fermi-contact ( $\mathcal{F}_{2,\beta}^I$ ) and spin-dipolar ( $\mathcal{F}_{3,\beta}^I$ ) terms [13]. The bilinear term is  $B_\alpha \mathcal{D}_{\alpha\beta}^I \mu_\beta^I$ , where the time-even operator  $\mathcal{D}_{\alpha\beta}^I$  describes diamagnetic shielding in closed-shell molecules [5, 13].

The thermally averaged field at the position of nucleus  $I$  is obtained by averaging the total hyperfine field:

$$\langle B_{\text{ind},\beta}^I \rangle = - \frac{\text{Tr}[\rho(\mathcal{F}_\beta^I + B_\alpha \mathcal{D}_{\alpha\beta}^I)]}{\text{Tr} \rho}, \quad (2)$$

where  $\rho = \exp[-\tilde{\beta}(H_0 + \mathcal{H}_z)]$  is the density operator and  $\tilde{\beta} = (k_B T)^{-1}$ . Next, we expand  $\rho$  to first order in  $\mathcal{H}_z$  [11, 14] and retain those terms of Eq. (2) that are linear

in  $B_\alpha$ . The result is expressed as a sum over the energy levels  $n$  (with degeneracy  $\omega_n$ ) of  $H_0$ :

$$\langle \sigma_{\alpha\beta}^I \rangle = \frac{1}{Z_0} \sum_n e^{-\tilde{\beta}\varepsilon_n} \text{Tr} \left[ \tilde{\beta} P_n \mu_{e,\alpha} P_n \mathcal{F}_\beta^I P_n + P_n \mathcal{D}_{\alpha\beta}^I P_n - P_n \mu_{e,\alpha} \frac{Q_n}{\varepsilon_n - H_0} \mathcal{F}_\beta^I P_n - P_n \mathcal{F}_\beta^I \frac{Q_n}{\varepsilon_n - H_0} \mu_{e,\alpha} P_n \right] \quad (3)$$

where  $P_n = \sum_{i=1}^{\omega_n} |n i\rangle \langle n i|$  is the projector on level  $n$ ,  $Q_n = 1 - P_n$ , and  $Z_0 = \sum_n \omega_n e^{-\tilde{\beta}\varepsilon_n}$ . This general expression for the shielding tensor formally resembles the Van Vleck equation for magnetic susceptibility [15].

A common situation consists of a system with only one thermally occupied degenerate energy level. The shielding tensor of such system can be decomposed as  $\langle \sigma \rangle = \sigma^p + \sigma^r$ , where the index  $I$  has been dropped to ease the notation. The temperature-independent term  $\sigma^r$  is universal to degenerate and non-degenerate states alike, and is known as the Ramsey shielding in the latter case. The effect of degeneracy is to shift  $\sigma^r$  by a temperature-dependent amount  $\sigma^p$ , the *paramagnetic shift*, which will be the focus of this Letter, and which, from Eq. (3), can be expressed as ( $P_0$  is the projector on the ground state):

$$\sigma_{\alpha\beta}^p = \frac{\tilde{\beta}}{\omega} \text{Tr}(P_0 \mu_{e,\alpha} P_0 \mathcal{F}_\beta P_0). \quad (4)$$

In Ref. [7],  $\sigma_{\alpha\beta}^p$  was calculated from the parameters of an EPR spin Hamiltonian, expressed in the usual way as  $\mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$ . However, this approach is only correct if  $S \leq 1$ , i.e., for 3-fold and 2-fold electronic degeneracies, but it is only an approximation for higher spin. [16] Moreover, while the approximation works for pure spin states, definition of spin Hamiltonians in the strong SOC limit needs additional caution.

To describe the strong coupling case we have in fact to resort to the concept of *fictitious spin*, and regard the degenerate manifold as a spin multiplet  $S$ , so that  $2S + 1 = \omega$ . Once the  $\omega$  wavefunctions of the ground manifold have been optimized via ab initio methods, the  $\omega \times \omega$  matrix representation  $\mathbf{X}$  of *any* operator  $X$  in the basis of these wavefunctions can be reproduced by an effective operator in the spin space [16], sum over irreducible tensor operators  $S_q^{(k)}$  of rank  $k$ , with spherical components  $q = -k, \dots, k$  labelled by Latin indices:

$$\mathbf{X} = \sum_{k=0}^{2S} \sum_{q=-k}^k (-1)^q X_q^{(k)} \mathbf{S}_{-q}^{(k)}. \quad (5)$$

Here the matrices  $\mathbf{S}_{-q}^{(k)}$ , representation of  $S_{-q}^{(k)}$  on the fictitious spin basis, form an orthogonal basis for the vector space of all complex square matrices of dimension  $2S + 1$ . The coefficients  $X_q^{(k)}$  can thus be determined from the ab initio matrices  $\mathbf{X}$  by orthogonal projection:

$$X_q^{(k)} = \text{Tr} \left( \mathbf{S}_q^{(k)} \mathbf{X} \right) \frac{2k + 1}{\langle S || S^{(k)} || S \rangle^2} \quad (6)$$

Our first aim is to reformulate the Curie shielding tensor Eq. (4) in terms of spin Hamiltonian parameters valid in the strong SOC limit, as these parameters can be routinely measured in EPR, and computed via accurate ab initio methods. To this end, we apply Eq. (6) to spin-decompose the three components of the *microscopic* Zeeman and hyperfine “fields” appearing in Eq. (4), leading to three sets of  $X$ -numbers for each field. A numerical example of how a projection is carried out using Eq. (5) and Eq. (6) is reported in the EPAPS [23].

Following usual notation we name the resulting generalized EPR “tensors” collecting these sets of numbers  $g_{q\alpha}^{(k)}$  (Zeeman) and  $A_{q\alpha}^{(k)}$  (hyperfine). For  $k = 1$ , we obtain the usual EPR  $\mathbf{g}$ -tensor and  $\mathbf{A}$ -tensor previously considered [6, 7]. For a general degeneracy, and arbitrary SOC strength, we obtain:

$$P_0 \mu_{e,\alpha} P_0 = -\mu_B \sum_{kq} (-1)^q S_{-q}^{(k)} g_{q\alpha}^{(k)} \quad (7)$$

$$P_0 \mathcal{F}_\beta^I P_0 = \frac{1}{g_N \mu_N} \sum_{kq} (-1)^q S_{-q}^{(k)} A_{q\beta}^{(k)} \quad (8)$$

with  $k \leq 2S$  and odd [17], and  $g_N$  the  $g$ -factor of the nucleus in question.

Substituting these expressions in Eq. (4) yields

$$\sigma_{\alpha\beta}^p = -\frac{\mu_B}{g_N \mu_N} \frac{\tilde{\beta}}{2S + 1} \sum_{kq} g_{q\alpha}^{(k)} A_{q\beta}^{(k)*} \frac{\langle S || S^{(k)} || S \rangle^2}{2k + 1}. \quad (9)$$

This expression generalizes all formulas previously proposed in the literature to the strong spin-orbit coupling limit, and to arbitrary degeneracy, thus representing one of the main results of this Letter. Interestingly, only products of same-rank tensors enter Eq. (9).

Next, we look for an expression for  $\sigma^p$  that is more general than Eq. (9), accounting for a time-even perturbation  $H_1$  that weakly splits the  $2S + 1$  degeneracy, which represents a common situation (see Figure 1). In cubic symmetry  $H_1$  may describe the vibronic coupling of a  $\Gamma_8$  electronic state to a Jahn-Teller active mode. For a pure spin degeneracy ( $S \geq 1$ ) [7],  $H_1$  leads to the EPR zero-field splitting (ZFS) Hamiltonian.

The same arguments [16] leading to Eq. (7) and Eq. (8) can be used to project  $H_1$  on the ground-manifold, irrespective of its microscopic origin, and map it into a spin Hamiltonian. This leads to  $P_0 H_1 P_0 = \sum_{k,q} (-1)^q D_q^{(k)} S_{-q}^{(k)}$ , where  $k$  is an even integer [17] ( $k \leq 2S$ ), and the generalized “ZFS tensors”  $D_q^{(k)}$  are evaluated via Eq. (6). For instance, the projector  $P_0$  on an ab initio  $\Gamma_8$  ground manifold is  $P_0 = \sum_q |q\rangle \langle q|$ , where  $q = \kappa, \lambda, \mu, \nu$  [18]. The rotational properties of a spin basis quantized along a  $C_4$  axis ( $Z$ ) readily lead to the mapping [18]:  $|\kappa\rangle \rightarrow |3/2\rangle$ ,  $|\lambda\rangle \rightarrow |1/2\rangle$ ,  $|\mu\rangle \rightarrow |-1/2\rangle$ ,  $|\nu\rangle \rightarrow |-3/2\rangle$ , and, for an axial distortion, to the spin Hamiltonian  $P_0 H_1 P_0 \equiv D(S_Z^2 - 5/4)$ , where

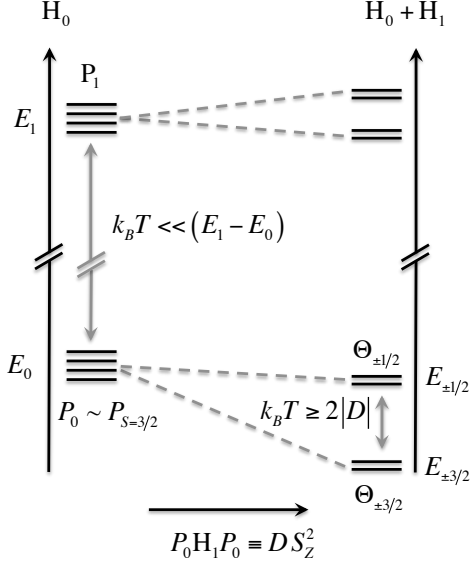


FIG. 1. Scheme of an axially split  $\Gamma_8$  ground state and associated projectors (see text). Left:  $\Gamma_8$  ground state (GS) of  $H_0$ , with ab initio projector  $P_0$  mapped to a spin ( $S = 3/2$ ) projector  $P_{S=3/2}$ . Right: splitting induced by  $H_1$ , described in GS by the spin Hamiltonian  $P_0 H_1 P_0 \equiv D S_Z^2$ , whose eigenfunctions define the split projectors  $\Theta_{\pm 3/2} = |3/2\rangle\langle 3/2| + |-3/2\rangle\langle -3/2|$ ,  $\Theta_{\pm 1/2} = |1/2\rangle\langle 1/2| + |-1/2\rangle\langle -1/2|$ .

$D = \langle \kappa | H_1 | \kappa \rangle = \langle \nu | H_1 | \nu \rangle = -\langle \lambda | H_1 | \lambda \rangle = -\langle \mu | H_1 | \mu \rangle$ . The paramagnetic shift for a split manifold can now be obtained only using the spin basis, via three simple steps.

First, we diagonalize the  $\omega \times \omega$  spin Hamiltonian  $P_0 H_1 P_0$ , and find the states  $|\psi_{\lambda a}\rangle$  and split energies  $\epsilon_{\lambda}$ , where  $\lambda = 1, \dots, \omega'$  ( $\omega' \leq 2S + 1$ ) labels the new low-lying degenerate manifolds, while  $a$  spans a single manifold. Next, the eigenstates  $|\psi_{\lambda a}\rangle$  are used to build new spin projectors  $\Theta_{\lambda} = \sum_a |\psi_{\lambda a}\rangle\langle \psi_{\lambda a}|$ , each associated to a degenerate manifold  $\lambda$ . For the axially split  $\Gamma_8$  case, as illustrated in Figure 1,  $D S_Z^2$  is diagonal,  $\Gamma_8$  splits into 2 Kramers doublets (KD), and the new spin projectors can be written as ( $D < 0$ )  $\Theta_{\pm 3/2}$  for the ground KD, and  $\Theta_{\pm 1/2}$  for the excited KD (see caption to Figure 1). Finally, the third step to obtain the paramagnetic shift for the split case is to apply Eq. (3), but instead of microscopic Hamiltonians and projectors, we now use the generalized Zeeman and hyperfine *spin Hamiltonians* ( $P_0 \mu_{e,\alpha} P_0$  and  $P_0 \mathcal{F}_{\beta}^I P_0$ ), and, crucially, the *spin projectors* defined on the split manifold ( $\Theta_{\lambda}$ ).

Following this strategy the paramagnetic shift of a split manifold can be solely expressed as function of  $g^{(k)}$  and  $A^{(k)}$  tensors, the rank  $k$  referring to the  $(2S+1)$ -manifold:

$$\sigma_{\alpha\beta}^p = \frac{\mu_B}{g_N \mu_N} \frac{1}{Z_0} \sum_{kq, k'q'} (-1)^{q+q'} g_{q\alpha}^{(k)} \mathcal{Q}_{qq'}^{kk'}(T) A_{q'\beta}^{(k')}, \quad (10)$$

where the partition function is defined over the split manifold as  $Z_0 = \sum_{\lambda} \omega_{\lambda} e^{-\beta \epsilon_{\lambda}}$ , and the non-trivial temperature dependent factor  $\mathcal{Q}_{qq'}^{kk'}(T) = \mathcal{Q}_{kq, k'q'}^{(1)} + \mathcal{Q}_{kq, k'q'}^{(2)}$ :

$$\mathcal{Q}_{kq, k'q'}^{(1)} = -\tilde{\beta} \sum_{\lambda=1}^{\omega'} e^{-\tilde{\beta} \epsilon_{\lambda}} \text{Tr} \left( \Theta_{\lambda} S_{-q}^{(k)} \Theta_{\lambda} S_{-q'}^{(k')} \Theta_{\lambda} \right) \quad (11)$$

$$\mathcal{Q}_{kq, k'q'}^{(2)} = \sum_{\substack{\lambda=1 \\ \mu \neq \lambda}}^{\omega'} e^{-\tilde{\beta} \epsilon_{\lambda}} \frac{2\Re \left[ \text{Tr} \left( \Theta_{\lambda} S_{-q}^{(k)} \Theta_{\mu} S_{-q'}^{(k')} \Theta_{\lambda} \right) \right]}{(\epsilon_{\lambda} - \epsilon_{\mu})} \quad (12)$$

Note that Eq. (10) is different from the ZFS-expression proposed in Ref. [7], in that (i) it depends on all possible products of tensors of all ranks allowed by the size of the degenerate manifold (ii) the “Curie term”, Eq. (11), cannot be written in terms of averaged products of spin operators as  $\langle S_q^{(k)} S_{q'}^{(k')} \rangle$  (iii) Eq. (10) contains a new “orbital” term, Eq. (12), giving rise to a non-Curie temperature dependence. The new term is essential to achieve the correct high-temperature limit, i.e. Eq. (9). Eq. (10), generalization of Eq. (9) to weak-split degeneracies, is the other main result of this Letter.

*Applications.* We illustrate the theory by evaluating the NMR paramagnetic shift of strong spin-orbit coupled dopant lanthanide nuclei in fluorite crystals, generally denoted as  $\text{CaF}_2:\text{Ln}$ . Among the Ln-ions occupying a cubic crystal site  $\text{Pr}^{2+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ , and  $\text{Dy}^{3+}$  are known to have a 4-fold degenerate ground state [19, 26], with symmetry  $\Gamma_8$  in the cubic double group  $O^*$ . Our theory is essential to correctly describe NMR for these nuclei.

Associating the  $\Gamma_8$  states to a spin  $S = 3/2$  as seen previously, from Eq. (7) and Eq. (8) one obtains:

$$P_0 \mu_{e,\alpha} P_0 = -\mu_B (g S_{\alpha} + g' W_{\alpha}) \quad (13)$$

$$P_0 \mathcal{F}_{\alpha}^I P_0 = \frac{1}{g_N \mu_N} (A S_{\alpha} + A' W_{\alpha}), \quad (14)$$

where

$$W_{\alpha} = 5 S_{\alpha}^3 - \frac{41}{4} S_{\alpha}, \quad \alpha = x, y, z \quad (15)$$

are the components of  $S^{(3)}$  that transform as a vector under octahedral symmetry [20]. Symmetry reduces the number of non-zero tensor components to just four, denoted by  $g$ ,  $g'$ ,  $A$ , and  $A'$ . Next, by means of Eq. (9), the paramagnetic shielding tensor (diagonal and isotropic in this symmetry) can be expressed as

$$\sigma^p = -\frac{\mu_B}{g_N \mu_N} \tilde{\beta} \frac{15}{4} \left( \frac{gA}{3} + 3g'A' \right) \quad (16)$$

To calculate  $\sigma^p$  via Eq. (16), we need the relevant rank-1 ( $g$  and  $A$ ) and rank-3 ( $g'$  and  $A'$ ) tensor components. We choose the multiconfigurational wave function method CASSCF, followed by a non-perturbative

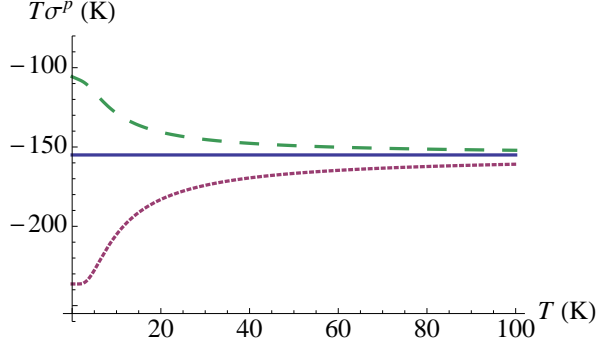


FIG. 2. (color online) Plot of  $\sigma^P T$  vs.  $T$  for the Nd impurity nucleus in  $\text{CaF}_2:\text{Nd}^{3+}$  crystal computed using the values in Table I. The solid (blue) line corresponds to  $\sigma^P T$  for an exact  $\Gamma_8$  ground state. The dotted (red) and dashed (green) curves correspond to  $\sigma_{\parallel}^P T$  and  $\sigma_{\perp}^P T$ , respectively, for an axially split ( $D = -5 \text{ cm}^{-1}$ )  $\Gamma_8$  state, calculated using Eq. (17).

calculation of the SOC as implemented in the code MOLCAS [21]. The Ln-impurity and its first coordination sphere ( $\text{LnF}_8^{q-}$ ) are treated as an ab initio fragment embedded in the  $\text{CaF}_2$  crystal potential, which is described by a combination of ab initio model potentials (AIMP) [22] and point charges in a finite cube centered on the Ln-ion (see EPAPS [23] for further details).

The ab initio matrix elements of the magnetic moment in the  $\Gamma_8$  ground state were used to determine  $g$  [24] and  $g'$ . Unfortunately, the calculation of the hyperfine constants is currently out of reach of the CASSCF method for most systems. Hence we chose to evaluate  $A$  and  $A'$  by assuming that  $A/g = A'/g' = A_J/g_J$ , where  $g_J$  and  $A_J$  are the free-ion Landé factor and hyperfine constant. This relation is exact in the limit of negligible  $J$ -mixing [25], arguably a good approximation for Ln-complexes. Estimating  $A_J/g_J$  from tabulated experiments [25, 26] allows us to obtain  $A$  and  $A'$  from the computed values of  $g$  and  $g'$ . All results are in Table I. The ab initio  $g$  values for  $\text{Pr}^{2+}$  and  $\text{Dy}^{3+}$  compare reasonably well with available EPR data:  $g_{\text{exp}} = -0.881$  and  $g'_{\text{exp}} = -0.173$  ( $\text{Pr}^{2+}$ ) [26],  $g_{\text{exp}} = 4.4$  and  $g'_{\text{exp}} = 0.19$  ( $\text{Dy}^{3+}$ ) [19]. Note that contributions arising from higher order EPR tensors ( $g'$  and  $A'$ ) in  $\text{CaF}_2:\text{Nd}^{3+}$  ( $\text{CaF}_2:\text{Pr}^{2+}$ ) account for 54% (46%) of the shielding tensor [27].

Finally, if the cubic environment of the impurity undergoes Jahn-Teller axial distortion along  $z$ , described by the ZFS fictitious spin Hamiltonian  $D(S_z^2 - 5/4)$ , application of Eq. (10), leads to the following components of

TABLE I. Ab initio (CASSCF) EPR parameters and NMR paramagnetic shift in the  $\Gamma_8$  ground state of  $\text{CaF}_2:\text{Ln}^{n+}$ , compared with available experimental data. The hyperfine constants ( $10^{-2} \text{ cm}^{-1}$ ) are divided by the nuclear  $g_N$  factor to make them isotope-independent. Values of  $T\sigma^P$  (K) are obtained from Eq. (16). In parenthesis we report the ab initio shift that would be obtained if  $g'$  and  $A'$  were neglected.

	$g$	$g'$	$A/g_N$	$A'/g_N$	$T\sigma^P$	$T\sigma^P(\text{exp})$
$\text{Pr}^{2+}$	-0.799	-0.245	-2.17	-0.666	-106 (-57)	-94 <sup>a</sup>
$\text{Nd}^{3+}$	-0.802	-0.293	-2.66	-0.971	-155 (-71)	-
$\text{Sm}^{3+}$	-0.233	-0.0632	-2.77	-0.754	-36 (-21)	-
$\text{Dy}^{3+}$	4.257	0.198	6.05	0.281	-867 (-850)	-906 <sup>a</sup>

<sup>a</sup> Calculated from EPR data reported in Ref. [19, 26]

the anisotropic Ln-shielding tensor in the split- $\Gamma_8$  state:

$$\begin{aligned}
 \sigma_{\parallel}^P &= -\frac{\mu_B}{g_N \mu_N} \frac{\tilde{\beta}}{\mathcal{Z}_0} \left\{ \frac{9}{2} (g + g') (A + A') \right. \\
 &\quad \left. + \frac{e^{-2\tilde{\beta}|D|}}{2} (g - 9g') (A - 9A') \right\} \\
 \sigma_{\perp}^P &= -\frac{\mu_B}{g_N \mu_N} \frac{\tilde{\beta}}{\mathcal{Z}_0} \left\{ \frac{225}{8} g' A' \right. \\
 &\quad \left. + \frac{e^{-2\tilde{\beta}|D|}}{8} (4g + 9g') (4A + 9A') \right\} \\
 &\quad - \frac{\mu_B}{g_N \mu_N} \frac{\tanh(\tilde{\beta}|D|)}{16|D|} \times \\
 &\quad \times 3 (2g - 3g') (2A - 3A')
 \end{aligned} \tag{17}$$

Note that in Eq. (17) products of tensors of different ranks appear, and the last term of  $\sigma_{\perp}^P$  is the new “orbital” contribution Eq. (12). Figure 2 shows the non-trivial temperature dependence of  $\sigma_{\parallel}^P$  and  $\sigma_{\perp}^P$  for the weakly split case, compared to the simple Curie term for a  $\Gamma_8$  ground state, in  $\text{CaF}_2:\text{Nd}^{3+}$ . This non-Curie behavior provides an experimental strategy to probe small interactions between nanomagnet and environment, by monitoring the paramagnetic shift as function of temperature.

In conclusion, we presented a general theory of NMR paramagnetic shifts, valid for arbitrarily degenerate electronic states. The shielding is a function of generalized EPR Zeeman and hyperfine tensors of all symmetry-allowed ranks. The significance of the approach has been demonstrated by high-level ab initio calculations. We believe the theory will be valuable to interpret pNMR data for lanthanide-based magnetic materials, and for the development of ab initio methods for pNMR.

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\* asoncini@unimelb.edu.au

- [1] *NMR-MRI,  $\mu$ SR and Mössbauer Spectroscopies in Molecular Magnets*, edited by P. Carretta and A. Lascialfari (Springer-Verlag, Milan, 2007).
- [2] I. Bertini, C. Luchinat, and G. Parigi, *Solution NMR of Paramagnetic Molecules* (Elsevier, Amsterdam, 2001).
- [3] A. Lascialfari, Z. H. Jang, F. Borsa, P. Carretta, and D. Gatteschi, Phys. Rev. Lett. **81**, 3773 (1998); P. Santini, S. Carretta, E. Livioti, G. Amoretti, P. Carretta, M. Filibian, A. Lascialfari, and E. Micotti, Phys. Rev. Lett. **94**, 077203 (2005); A. Bianchi, S. Carretta, P. Santini, G. Amoretti, J. Lago, M. Corti, A. Lascialfari, P. Arosio, G. Timco, and R. E. P. Winpenny, Phys. Rev. B **82**, 134403 (2010).
- [4] F. Branzoli, M. Filibian, P. Carretta, S. Klyatskaya, and M. Ruben, Phys. Rev. B **79**, 220404(R) (2009).
- [5] *Calculation of NMR and EPR Parameters. Theory and Applications*, edited by M. Kaupp, M. Bühl and V. G. Malkin, (Wiley-VCH, Weinheim, 2004).
- [6] S. Moon and S. Patchkovskii, Chapter 20 in Ref. [5].
- [7] T. O. Pennanen and J. Vaara, Phys. Rev. Lett. **100**, 133002 (2008).
- [8] Z. Rinkevicius, J. Vaara, L. Telyatnyk, and O. Vahtras, J. Chem. Phys. **118**, 2550 (2003).
- [9] A. Soncini, J. Chem. Theory Comput. **3**, 2243 (2007).
- [10] J. Autschbach, S. Patchkovskii and B. Pritchard, J. Chem. Theory Comput. **7**, 2175 (2011).
- [11] R. J. Kurland and B. R. McGarvey, J. Magn. Reson. **2**, 286 (1970).
- [12] Use of relativistic operators, more appropriate for heavy elements, would not affect the validity of this theory.
- [13] A. Abragam, *The principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961), pp.176–177.
- [14] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).
- [15] M. Gerloch and R. F. McMeeking, J. Chem. Soc. Dalton Trans. 2443 (1975).
- [16] J. S. Griffith, Mol. Phys. **3**, 79 (1960); Phys. Rev. **132**, 316 (1963).
- [17] But note that  $k$  can be both even and odd for a manifold of even degeneracy in an even-electron system [16].
- [18] J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, Cambridge, 1961), Table A 19.
- [19] M. J. Weber and R. W. Bierig, Phys. Rev. **134**, A1492 (1964).
- [20] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, Oxford, 1970), p. 723.
- [21] F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P.-Å Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitonak, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, and R. Lindh, J. Comput. Chem. **31**, 224 (2010).
- [22] J. L. Pascual and L. Seijo, J. Chem. Phys. **102**, 5368 (1995).
- [23] For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
- [24] L. Chibotaru, A. Ceulemans and H. Bolvin, Phys. Rev. Lett. **101**, 033003 (2008).
- [25] Ref. [20], pp. 296–298.
- [26] E. R. Bernstein and L. W. Dennis, Phys. Rev. B **20**, 870 (1979).
- [27] Our theory can be relevant for d-electrons as well. Octahedral Ti(III) has a  $\Gamma_8$  ground state, where  $g = g' = 0$  (see [18], p. 271), but mixing of the excited  $E_g$  configuration by SOC in first order leads to  $g = -g' = \frac{4}{5} \left( \frac{\zeta}{\Delta} \right)$ , where  $\zeta$  is the SOC constant and  $\Delta$  the crystal field splitting (i.e.  $g = -g' \approx 10^{-2}$ ). In this case our theory is clearly needed to estimate the correct pNMR shift.